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**Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals**

**Sub-Committee of Experts on the Transport of Dangerous Goods**

**Fifty-third session**
Geneva, 25 June-4 July 2018
Item 10 (b) of the provisional agenda
**Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: testing of oxidizing substances**

**Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals**

**Thirty-fifth session**
Geneva, 4-6 July 2018
Item 3 (a) of the provisional agenda
**Classification criteria and related hazard communication: work of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG) on matters of interest to the GHS Sub-Committee**

# Tests for oxidizing liquids (Test O.2) and oxidizing solids (Tests O.1 and O.3): Consequential amendments of cellulose replacement to test descriptions

**Transmitted by the expert from France***

## Introduction

1. During its eighth session, the Committee approved the programme of work of its two sub-committees for the biennium 2017-2018 (see ST/SG/AC.10/44, para 14; ST/SG/AC.10/C.3/100, para 98; ST/SG/AC.10/C.4/64, annex III). This programme of work includes among issues relating to the GHS, testing of oxidizing substances.

2. This programme of work will focus on consequential amendments to Test O.1 to O.3 as a follow-up of the replacement of cellulose as agreed by the Committee (see

* In accordance with the programme of work of the Sub-Committee for 2017-2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, paragraph 98 and ST/SG/AC.10/44, para. 14)

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ST/SG/AC.10/44, para 11 and /Add. 2, section 34; ST/SG/AC.10/C.3/100, para 79-82; ST/SG/AC.10/C.3/64, para 14).

3. The calendar for the development of the consequential amendments to Test O.1 to O.3 as a follow-up of the replacement of cellulose indicated by the expert from France in ST/SG/AC.10/C.3/2017/28 has been applied.

4. An overview of the progress of work was given in ST/SG/AC.10/C.3/2017/45 and informal document INF.35 (fifty-second session) as well as first proposals for amendments of the test descriptions for oxidizing liquids (Test O.2) and oxidizing solids (Test O.1 and O.3).

## Results of the programme of work

5. The following paragraphs give the results of the work carried out for the four items identified for consideration (see informal document INF.12 (fifty-first session)) in the programme of work.

6. For the improvement of Test O.2, it was first considered the possibility of replacement of the reference substances for allocation of packing group (PG) II (i.e. 40% aqueous sodium chlorate solution) and of PGIII (i.e. 65% aqueous nitric acid) by diluted aqueous solutions of perchloric acid[1] in the range of 30-40%. Preliminary promising results were presented by the French National Institute for Industrial Environment and Risk (INERIS) to other laboratories in September. Although most of the laboratories expressed their sympathy for the idea of replacing three reference substances by only one in the test method, it was also recognized that this operation will required additional work and a longer time frame before it can be validated through Round Robin Tests (RRT).

7. Secondly it was considered to improve the wording of the test description, in particular of the section 34.4.2.3 of the Manual of Tests and Criteria, (ST/SG/AC.10/11/Rev.6). For that a questionnaire was circulated between the nine laboratories that participated to a RRT (see informal document INF.47 (forty-ninth session) annex 1) on Test O.2 in 2015 to collect details of their best practices. Feedback gained from their answers and other communication allow to make a proposal (see para 13 of this document).

8. The reference oxidizer (i.e. calcium peroxide 75%) for Test O.3 may originate from different sources and is subject to ageing. Therefore, the question of the necessity of a determination of the concentration in calcium peroxide prior using the reference oxidizer was investigated. It was judged that making this determination mandatory prior to each testing campaign would increase the level of complexity of Test O.3 methodology, require further interlaboratory studies and create an unnecessary burden. It was considered that the quality of the calcium peroxide shall be based on the certificate of analysis from the supplier and its date of expiry. It was also recognized that the tolerance given for the concentration of calcium peroxide as specification could be changed with no impact on the outcome of the test and that will extend the period of usage of calcium peroxide according to the actual specifications of the suppliers. See corresponding proposal in para 14 of this document.

[1] A 50% aqueous solution of perchloric acid is already the reference substance for allocation of PGI

9. Requirements in Test O.3 description (see section 34.4.3.5.3 of the Manual of Tests and Criteria ST/SG/AC.10/11/Rev.6) are set for the coefficient of correlation R2 (i.e. at least 0.95) and the standard deviation (i.e. not exceeding 10%). From a practical point of view, to respect the strictness of these criteria has for consequence the necessity to repeat burning trials a very numerous time before both criteria can be met at once.

10. Following a RRT on Test O.3 (see informal document INF.47 (forty-ninth session) annex 2) and analysis of its results, these criteria were, indeed, seen to be too limiting by the majority of the thirteen participating laboratories. The impact and consequence of a possible relaxation of these criteria were studied based on test results gained during the hereinbefore RRT. The study showed that no significant alteration of the overall results (i.e. classification of the tested substances) were noticeable in the case where the criteria are changed from "at least 0.95" to "at least 0.90" for the coefficient of correlation $R^2$ and from "not exceeding 10%" to "not exceeding 20%" for the standard deviation. See corresponding proposal in para 15 of this document.

11. During Test O.3 in some cases breakage of the wire during the runs is observed see for illustration the RRT report detailed in informal document INF.47 (forty-ninth session) annex 2, para 2.5.1.1. The possible reasons of these breakages were explored in more details by France. It is known from the literature[2] that this issue is more frequent with nitrate compounds or with low melting point samples. In this latter case, the melted portion of the sample may fuse to the ignition wire and the fused portion possibly reaches a temperature higher than the melting point of the ignition wire. Different natures of ignition wires are already used by the different laboratories. Information on the performance of these wires are available in a published RRT report and can be used as guidance for the selection of a wire on a case by case based on the laboratory experience. Based on that it is seen not necessary to change the specifications given in section 34.4.3.3.2.

12. For Test O.1 which is similar in principle to Test O.3, the wording for the metal wire description in 34.4.1.2.3 can be aligned with the text in 34.4.3.3.2 to benefit from the work achieved during the development of Test O.3. See corresponding proposal in para 16 of this document.

## Proposals for amendments

13. In the following proposals, new text is underlined and deleted text is ~~struck out~~.

## Proposal relating to Test O.2 – improved wording

14. Modify the text in the Test O.2 description, i.e. in section 34.4.2.3.1 of the Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.6, as follows:

> "34.4.2.3.1 The apparatus, assembled complete with pressure transducer and heating system but without the bursting disc in position, is supported firing plug end down. A leakage test should be conducted on an empty vessel beforehand. 2.50 ± 0.01 g of the liquid to be tested is mixed with 2.50 ± 0.01 g of dried cellulose in a glass beaker using a glass stirring rod or any other appropriate mixing tool for at least two minutes. The time for mixing should be tracked by a timer and kept uniform for all mixtures. **For safety, the mixing should be performed with a**

[2] Hiroshi Koseki in Journal of Loss Prevention in the Process Industries 14 (2001) 431–434

**safety shield between the operator and mixture.** (If the mixture ignites during mixing or filling, no further testing is necessary.) The mixture is added, in small portions with tapping, to the pressure vessel making sure that the mixture is packed around the ignition coil and is in good contact with it. It is important that the coil is not distorted during the packing process and should be covered completely by the mixture after loading. The bursting disc is placed in position and the retaining plug is screwed in tightly. The charged vessel is transferred bursting disc uppermost to the firing support stand, ~~bursting disc uppermost~~, which should be located in a suitable, armoured fume cupboard or firing cell. The power supply is connected to the external terminals of the firing plug and 10 ± 0.5 A applied. The electric power is set before loading the vessel and should remain fixed for each test sequence or until any breakage of the wire occurs. The time between the start of mixing and switching the power on should ~~be about 10 minutes~~ be as short as possible and be kept constant for each test series.

## Proposal relating to Test O.3 – Reference oxidizer

15. Modify the text in the Test O.3 description, i.e. in section 34.4.3.2.1 of the Manual of Tests and Criteria, (ST/SG/AC.10/11/Rev.6), as follows:

"34.4.3.2.1 Technically pure, finely powdered calcium peroxide with a concentration of 75% ± ~~0.5~~ 1.0% is required as the reference oxidizer. The concentration of impurities such as chlorides or compounds which generate water during combustion should be low, as they may ~~impact~~ affect on the burning behavior of the reference ~~piles~~ mixtures. Calcium peroxide meeting the specification below can be used without further pretreatment.[4]

| | |
|---|---|
| $CaO_2$: | 75% ± ~~0.5~~ 1.0 % |
| $Ca(OH)_2$: | 20% to 25% |
| $CaCO_3$: | 0% to 5% |
| Chloride: | max 500 ppm |
| Particle size: | min 99% < 75 µm, ~~and thereof~~ of which |
| | min 50% < 20 µm" |

## Proposal relating to Test O.3 – Coefficient of correlation, standard deviation of test results and improved wording

16. Modify the text in the Test O.3 description, i.e. in section 34.4.3.5.3 of the Manual of Tests and Criteria, (ST/SG/AC.10/11/Rev.6), as follows:

"34.4.3.5.3 The burning rate (BR) depends on the burning intensity and the amount of cellulose in the mixture. ~~It is therefore~~ For the purpose of this test it is defined as the quotient of 60% of the total amount of cellulose ($m_{cellulose}$) in the conical pile and the main combustion time $t_{20\text{-}80}$. The time $t_{20\text{-}80}$ is the time between 20% and 80% of the total mass loss. The total mass loss is the difference in mass before ignition and at the end of the ~~main reaction~~ combustion, defined as the time after which the a rate of mass loss rate of less than 1 g per minute.
The burning rate $BR_{20\text{-}80}$ is therefore calculated by the following equation:

$$BR_{20-80} = \frac{0.6 \times m_{cellulose}}{t_{20-80}}$$

where:

$BR_{20\text{-}80}$ = burning rate between 20% to 80% in g/s
$m_{cellulose}$ = mass of cellulose in mixture in gram
$t_{20\text{-}80}$ = burning time between 20% to 80% of total mass loss in seconds

Five valid tests should be performed with each reference and test substance mixture. The profile of each burning test has to be examined by plotting the mass loss as a function of time. The graph can also be used for decision making and should be used in case of doubt. The coefficient of correlation ($R^2$) of the mass curve of each burning test should be at least ~~0.95~~ 0.90 between 20% to 80% mass loss, otherwise the burning trial has to be repeated. ~~Five valid tests should be performed with each reference and test substance mixture.~~ The standard deviation of the burning rates within these five tests should not exceed ~~10%~~ 20% in total. If these test quality criteria are not met due to test sample properties, judgement based on previous experience or competence of the person responsible for the classification should take precedence over recommended test criteria."

## Proposal relating to Test O.1 – Metal wire description

17. Modify the text in the Test O.1 description, i.e. in section 34.4.1.2.3 of the Manual of Tests and Criteria, (ST/SG/AC.10/11/Rev.6), as follows:

"34.4.1.2.3 An ignition source is required comprising an inert metal wire ~~(e.g. nickel/chromium)~~ connected to an electrical power source ~~and with the following characteristics~~ capable of maintaining the power dissipation specified below. The electrical resistance depends on the wire material[1]. It is recommended to use a nickel/chromium or Aluchrom wire as follows:

~~(a) Length = 30 ± 1 cm;~~
~~(b) Diameter = 0.6 ± 0.05 mm;~~
~~(c) Electrical resistance = 6.0 ± 0.5 Ω/m;~~
~~(d) Electrical power dissipated in the wire = 150 ± 7 W.~~

| | |
|---|---|
| (a) Length | = 30 cm ± 1 cm; |
| (b) Diameter | below 1 mm; |
| (c) Electrical power dissipated in the wire | = 150 W ± 7 W. |

The wire should be shaped as in Figure 34.4.1.1.".